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Analysis Method

Central composite design for the optimisation of Cd and Pb determination in PVC materials by atomic absorption spectrometry after Kjeldahl digestion

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ABSTRACT

A convenient and simple wet acid digestion method was developed for the determination of Cd and Pb concentrations in polyvinyl chloride matrices by atomic absorption spectrometry. Response surface methodology (RSM) was used to optimise the conditions for maximum recovery and to understand the significance and interaction of the factors affecting the recovery of Cd and Pb. The central composite design was employed to evaluate the effects of nitric acid volume (2.6–9.4 mL), sulphuric acid volume (0.6–7.4 mL) and certified reference material (CRM) amount (0.1–0.5 g) on the metal recoveries (60 min, 200 °C and 20 min, 250 °C). The accuracy was also evaluated using the polyvinyl chloride reference material Fluxana FLX-PVC2. The apparent recoveries of the elements relative to the certified values ranged from 0.94 (Cd) to 0.92 (Pb). The method's detection limits were found to be 1.6 and 6.4 mg kg^{-1} for Cd and Pb, respectively.

1. Introduction

Plastics are among the most important materials used in daily life and industry today, and the amount of plastic produced is still growing. Optimisation of the material properties can be achieved by using different additives. However, the elemental contents of plastic materials must not exceed the concentration limits specified by regulations, such as the Packaging & Packaging Waste Directive 94/62/EC, the Waste Electrical & Electronics Equipment (WEEE) Directive 2002/96/EC and the Restriction of the use of certain Hazardous Substances in Electrical & Electronics equipment (RoHS) Directive 2002/95/EC, which all regulate the maximum amount of heavy metals (Cd, Cr(VI), Hg and Pb) in different types of plastic materials [1–3]. These compounds might originate from flame retardants, antimicrobial reagents, plasticisers, heat stabilisers or pigments. Tin, lead and other organometallic compounds are added to poly(vinyl chloride) (PVC) to inhibit the dehydrochlorination of labile chlorine atoms.

The increasing needs of the plastic industry and its subsequent new regulations can be met only by improvements in the accuracy and precision of the analytical methods applied to plastic research. The sample preparation step to determine element contents in plastics depends on not only the measurement technique but also on the polymer type. For this reason, the sample preparation step has to be evaluated for each polymer type. The poor homogeneity of many samples and the lack of standard methods for plastics analysis are among the other problems [4]. Sample diversity in commonly applied methods for elemental analyses increases with higher interfering element concentrations; hence the validity of the analytical data must be confirmed by using Certified

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Reference Materials (CRMs) or by comparison of the results of independent analytical methods.

Numerous works have already dealt with the determination of toxic metal concentrations, mainly in polyethylene samples [5–8], by using atomic spectrometry, although optical analytical methods typically require the sample to be dissolved in an aqueous medium. Most conventional approaches are based on sample decomposition procedures, such as dry or wet ashing using high pressures, elevated temperatures and/or microwave (MW) assistance with inorganic acids prior to analysis with atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectroscopy or mass spectroscopy (ICP-AES/MS) techniques [4,8,9]. The application of MW systems shortens the time of sample decomposition, reduces the consumption of acids and is more reproducible than mineralisation in an open system. However, these systems have high acquirement cost.

Another approach is the direct analysis of solid samples using a solid sampling device [10–12] or laser ablation ICP-MS [13] and X-ray fluorescence (XRF) spectrometry [14,15]. These approaches have excellent sensitivity for trace element concentration determination in very small samples. However, homogeneity problems in plastic materials limit the usage of these methods.

A method based on a wet digestion procedure that avoids the disadvantages of open-vessel methods (loss of analytes, risk of contamination, time consuming) could be an adequate alternative for laboratories. However, expensive equipment and instrumentation is needed for closed-vessel methods. In open-vessel methods, the experimental design may contribute to optimising the factors of interest and to identifying the variables that influence such factors, thereby improving the performance of a given methodology or process. Proper experimental design can also facilitate estimation of the significance of different variables and decrease the number of experimental runs per variable, thus reducing the total time needed. Central composite design has been the most successful factorial design for the optimisation of parameters with a limited number of experiments and for estimates based on response surfaces. This type of approach using screening and optimisation design steps has been applied in the determination of cadmium levels in polyethylene samples by AAS [16] and the levels of multiple elements in certified reference plant materials by ICP-AES [17]. A three-level full factorial design has been used in the optimisation of microwave digestion for the determination of Ca, Fe, Mg, Cu, Ni, and Zr concentrations in ceramic samples [18]. Plackett-Burman designs have been used to evaluate the most important variables affecting the process, and central composite designs have been used to find the optimum conditions for microwave digestion to determine trace element concentrations in seafood products using AAS [19].

The aim of this study was to use the Kjeldahl method for digestion to avoid analyte losses for the determination of Cd and Pb concentrations in PVC matrices by AAS. To obtain the best experimental conditions for plastic digestion, a central composite design experiment was performed. The accuracy for the quantification of the mentioned elements was assessed using the Fluxana PVC-set reference material.

2. Experimental

2.1. Apparatus

A Varian AA 220 FS (Victoria, Australia) model AAS was used for atomic absorption measurements (Cd, Pb). This AAS was equipped with a single-slot burner head for air-acetylene flame AAS and a deuterium background correction system. The experimental conditions selected in the AAS analysis of the elements in plastics are given in Table 1.

A Tecator 2012 Digester (Hoganas, Sweden) model digestion apparatus with Kjeldahl flasks was used to dissolve the plastic samples. The system contained twelve Kjeldahl glass flasks (volume, 100 ml; height, 30 cm; diameter, 2.5 cm). All units had glass exhaust manifolds with funnel-shaped adapters that fit into the necks of the flasks, and a water cooling unit to eliminate vapour losses during the heating steps. The temperature program was 200 °C for 60 min and then 250 °C for 20 min.

2.2. Chemicals

All chemicals used were of analytical reagent grade. Water was purified using a GenPure UV-TOC/UV model ultapure water system equipped with UV-photooxidation, total organic carbon (TOC) and ultrafiltration modules (TKA Wasseraufbereitung-systeme GmbH, Niederelbert, Germany). The conductivity of the deionized water was <0.056 µS.

Concentrated nitric (purity 65%) and sulphuric acids were purchased from Merck (Darmstadt, Germany). Certified Reference Material Fluxana FLX-PVC-2 (Fluxana GmbH & Co.KG, Kleve, Germany) was used for method validation. This reference material is a polyvinyl chloride (PVC) with certified contents of several metals including Cd and Pb. AAS single element standard solutions of 1000 mg L^{-1} for Cd and Pb were obtained from Merck (Darmstadt, Germany).

2.3. Sample preparation

Approximately 100 mg of CRM was weighed and transferred into Kjeldahl flasks. After careful addition of 3 mL of concentrated HNO_3 and H_2SO_4, the flask was inserted into a digester block that held up to 12 vials. The block digester was used for Kjeldahl nitrogen determination. The sample in the acids was gently heated until the temperature reached 200 °C for 60 min, after which time the sample was heated to 250 °C and then maintained at this temperature for 20 min. The solution was left to cool and was then filtered. The filtrate was brought up to

Table 1
Experimental conditions in AAS analysis.

	Cd	Pb
Wavelength (nm)	228.8	217.0
Flame (air flow, l min^{-1})	13.5	13.5
Flame (acetylene flow, l min^{-1})	2.0	2.0
Slit width (nm)	0.5	1.0
Lamp Current (mA)	4.0	10.0